Low-Pt Hydrous Metal Oxides for Oxygen Reduction at PEMFC Cathodes

Karen Swider Lyons and Peter Bouwman

Naval Research Laboratory, Washington DC

Wojtek Dmowski

University of Tennessee, Knoxville, TN

2004 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review

Philadelphia PA 25 May 2004

FY04 Budget

FY03 Budget: $180 K
FY04 Budget: $200 K
Subcontractor: W. Dmowski, U Tenn: $50K/yr

- NRL Team:
  - Dr. Peter Bouwman (NRL/USNA) - electrochemistry
  - Dr. Wojtek Dmowski (U Tenn) - structural characterization
  - Prof. Dave Ramaker (NRL/GWU) - XANES analysis
  - Dr. Terry Schull (NRL) - Materials synthesis (paints and coatings!)
  - Ms. Norma Ugarte & Prof. Russ Chianelli (UTexas - El Paso)
    - continue work on Pt-SnO_x compound (FY03 support)
    - XANES analysis (Prof. George Meitzner)

Objective

lower Pt content & cost of PEMFCs

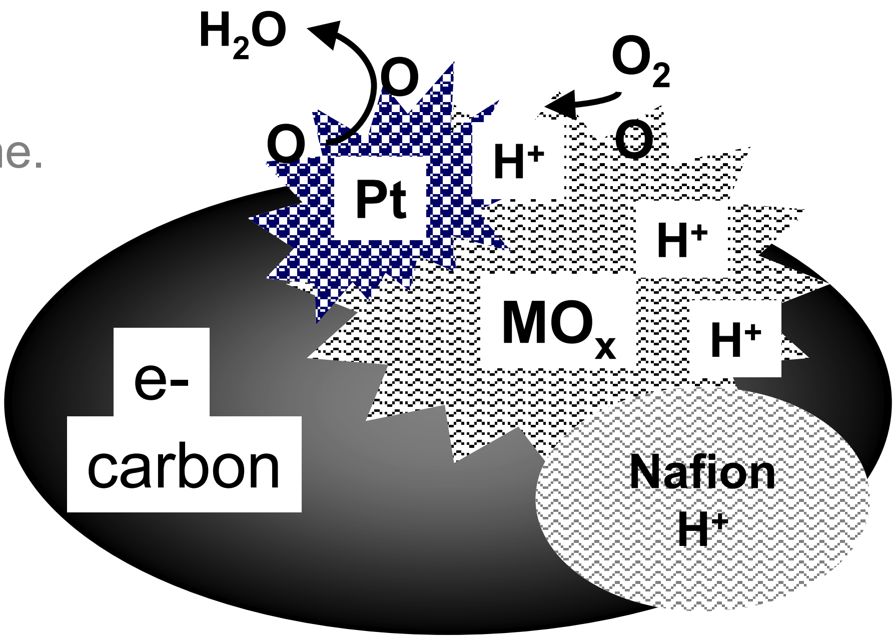
- Target DOE goals to achieve 0.02 g Pt/rated kW before 2010.
- Focus on lowering Pt in fuel cell cathode
- Cathode has most Pt because
  - slow oxygen reduction kinetics
  - poor Pt stability and ripening over time.

Utilize oxide-based supports for Pt and other metals to *leverage:*

- Oxygen dissociation by oxides
- Metal-support interactions with Pt
- Ionic mobility of oxide supports

2004 Objectives:

- "Perfect" electrochemical methods
- Rigorously characterize active and inactive catalysts
- Devise mechanism(s) to explain catalyst activity
- Design new active and stable catalysts.

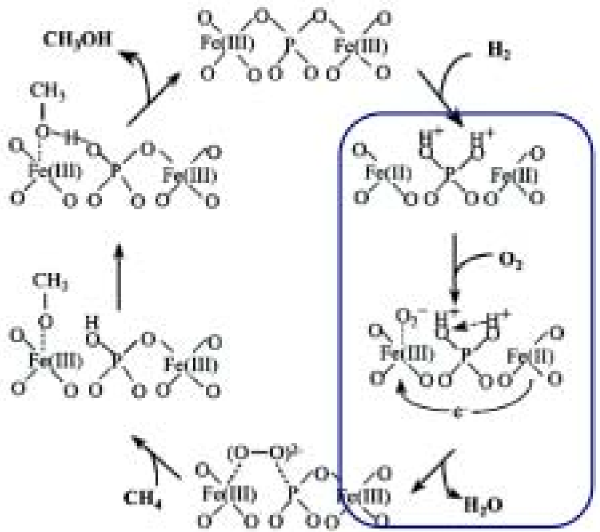


Pt supported on MO_x•H_2O supported on carbon

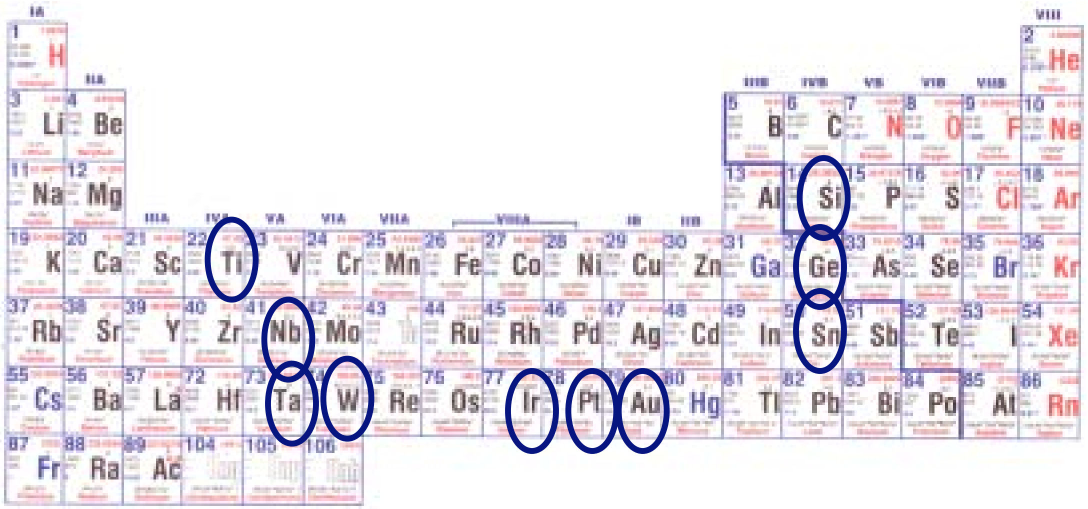
$$O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O$$

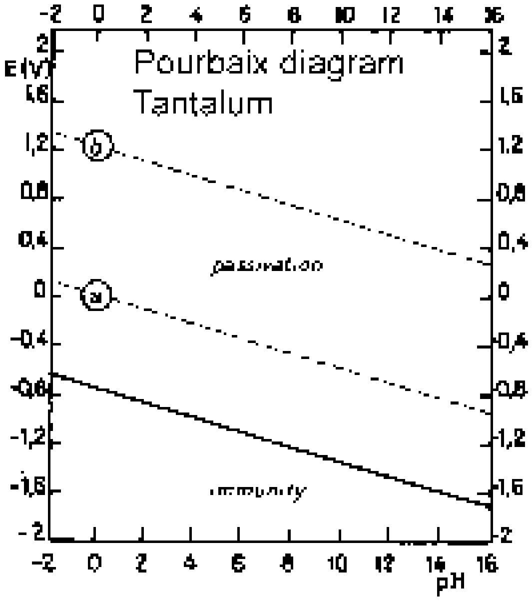
Approach - materials selection

Choose stable, active hydrous oxides/phosphates



Mechanism for partial oxidation of methanol with iron phosphate, K. Otsuka. Y. Wang Applied Catalysis A: General 222 (2001) 145-161





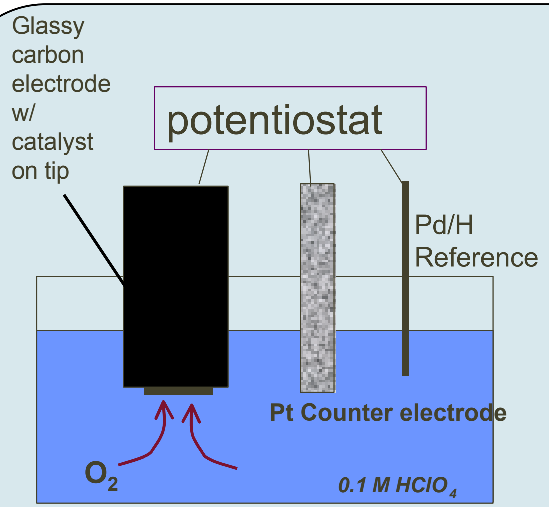
Select catalysts with high:

- ***activity for oxygen***
  - ***Partial oxidation catalysts***
- ***protonic conduction***
  - ***Hydrous oxides and phosphates***
- ***stability in acid***
  - ***use Pourbaix diagrams as guide***
  - ***some materials can be stabilized***

Approach: materials characterization

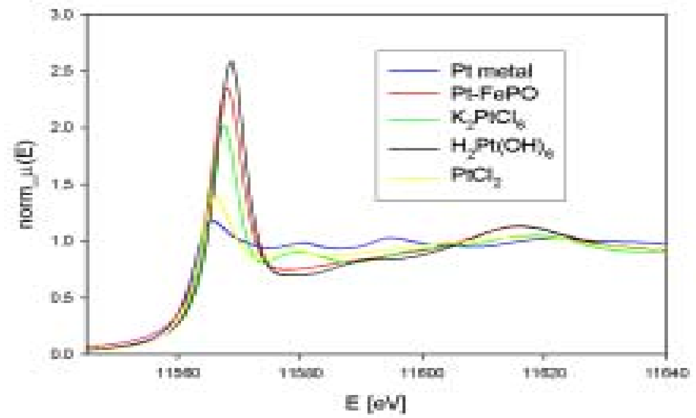
Electrochemical, physical and structural analysis

- Electrochemical evaluation
  - RDE - rotation disk electrodes
  - MEAs for fuel cells vs. Pt/VC anodes
- Physical characterization
  - BET, SEM, FTIR, TGA/DSC
- Oxidation states
  - XPS and XANES (in-situ and ex-situ)
- Structural analysis
  - XRD with PDF analysis

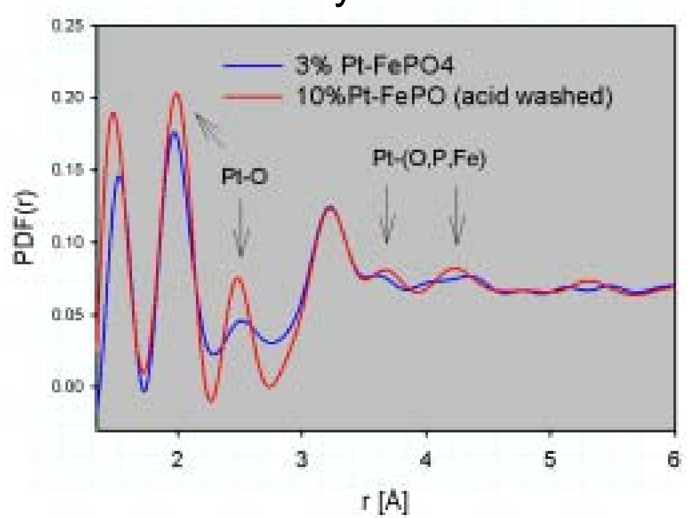


RDE method:
- Mix catalysts with Vulcan carbon & Nafion
- Disperse on RDE tip
- Evaluate in 0.1 M $HClO_4$ at 60 °C at 5 mV/s

In-situ and ex-situ XANES of Pt



Pair density function analysis of X-ray diffraction



Timeline

YEAR 1
April 1, 2001 - Start Program
Observe high activity of Pt-FePO materials (RDE)
Begin testing materials in fuel cells (unsuccessful)
Determine microporous structure with ionic Pt

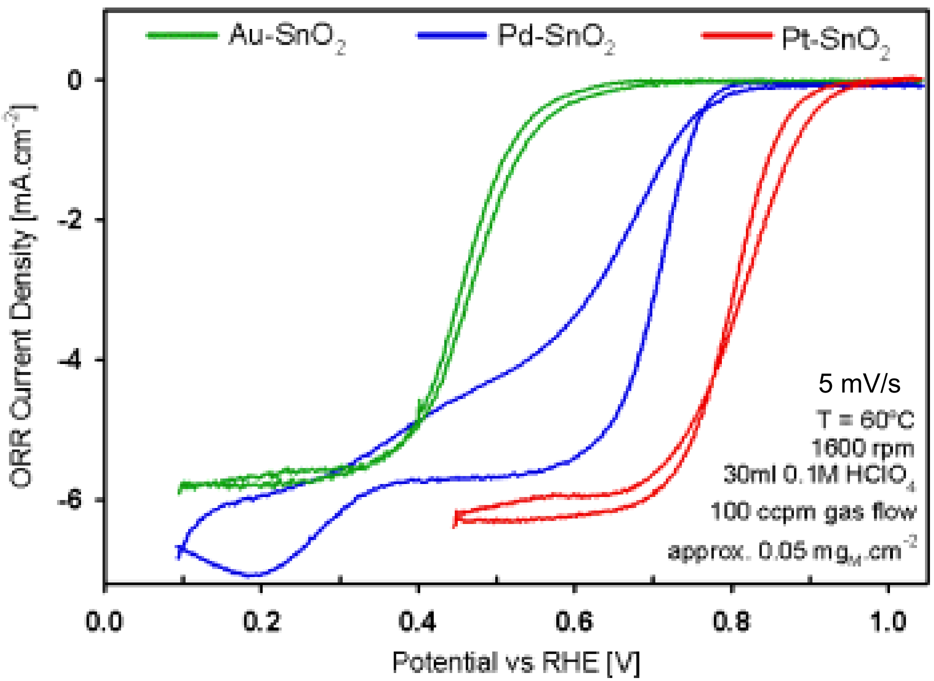
YEAR 2
Observe high activity of Pt-NbPOx samples (RDE)
Observe high activity of Pt-SnOx samples (RDE)
Acquire fuel cell test station (ONR support)
Observe high activity of Pt-SnOx catalysts in fuel cell operation
Successfully operate Pt-FePO in fuel cells
Establish chemical stability of Pt-FePO, Pt-NbPO, Pt-SnO_x

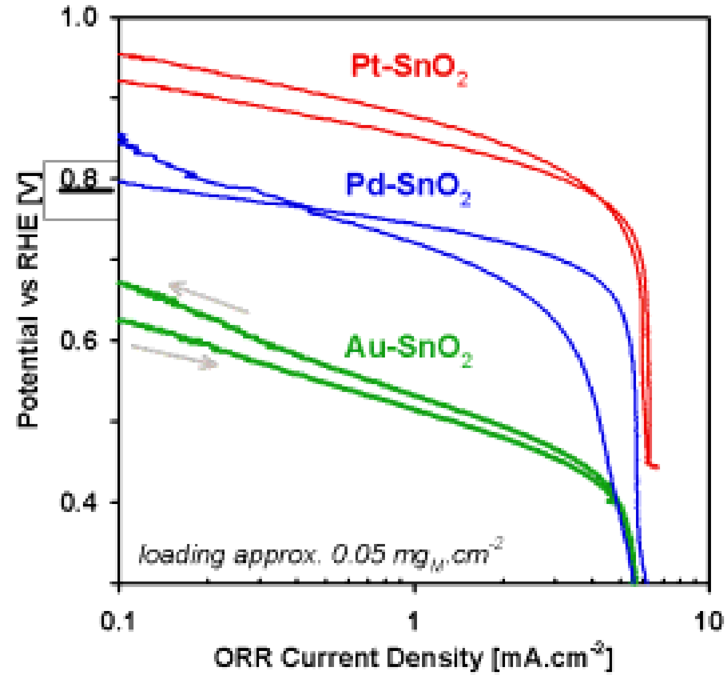
Year 3 - Activities and milestones

- Worked with GM Fuel Cell Activities (Gasteiger/Kocha) to improve testing methods
- Completed 2 in-situ XANES analyses of catalysts
- Milestone: Pt-$TaPO_x$ nanoparticles with 2 to 3x activity of Pt/VC standard
- Milestone: Pt-SnO_x impregnated with non-Pt metals show high ORR activity

Accomplishments

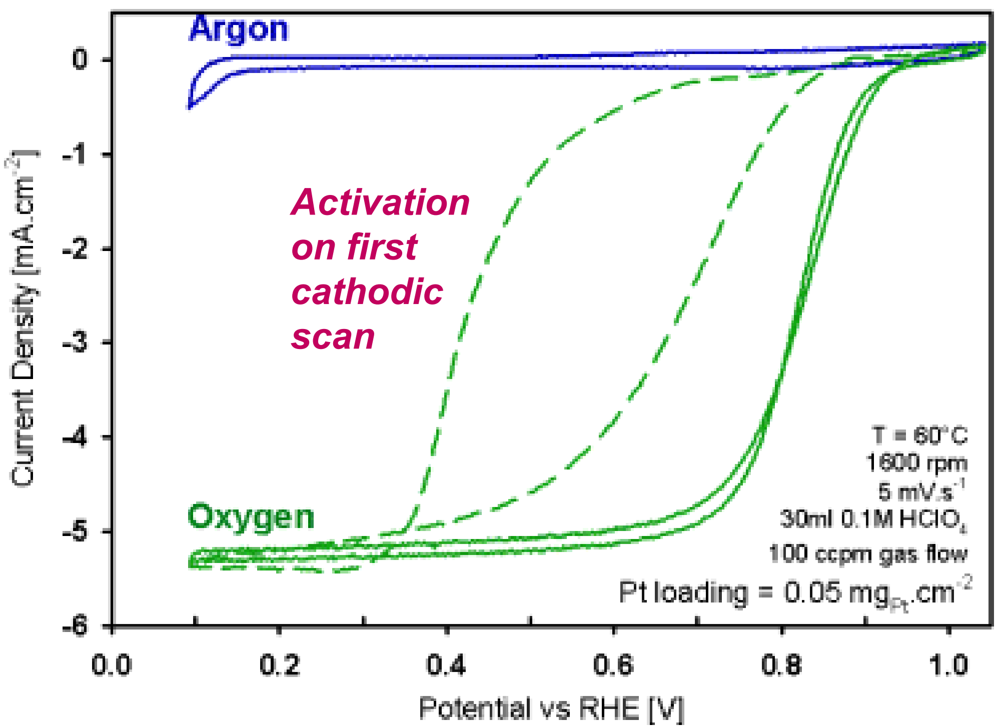
Track improved ORR of metals on hydrous SnO_x





- Ion exchange hydrous SnO with various metals
- Catalysts oxidized to Sn^{4+} during heating or electrochemically (in case of Au)
- Enhanced ORR activity for Au and Pd on SnOx
  - Pt shown above lower than expected due to Cl^- contamination
- XANES/XRD analysis needed to determine oxidation states and/or particle-size of metals

Accomplishments
High-activity Pt-Tantalum Phosphates



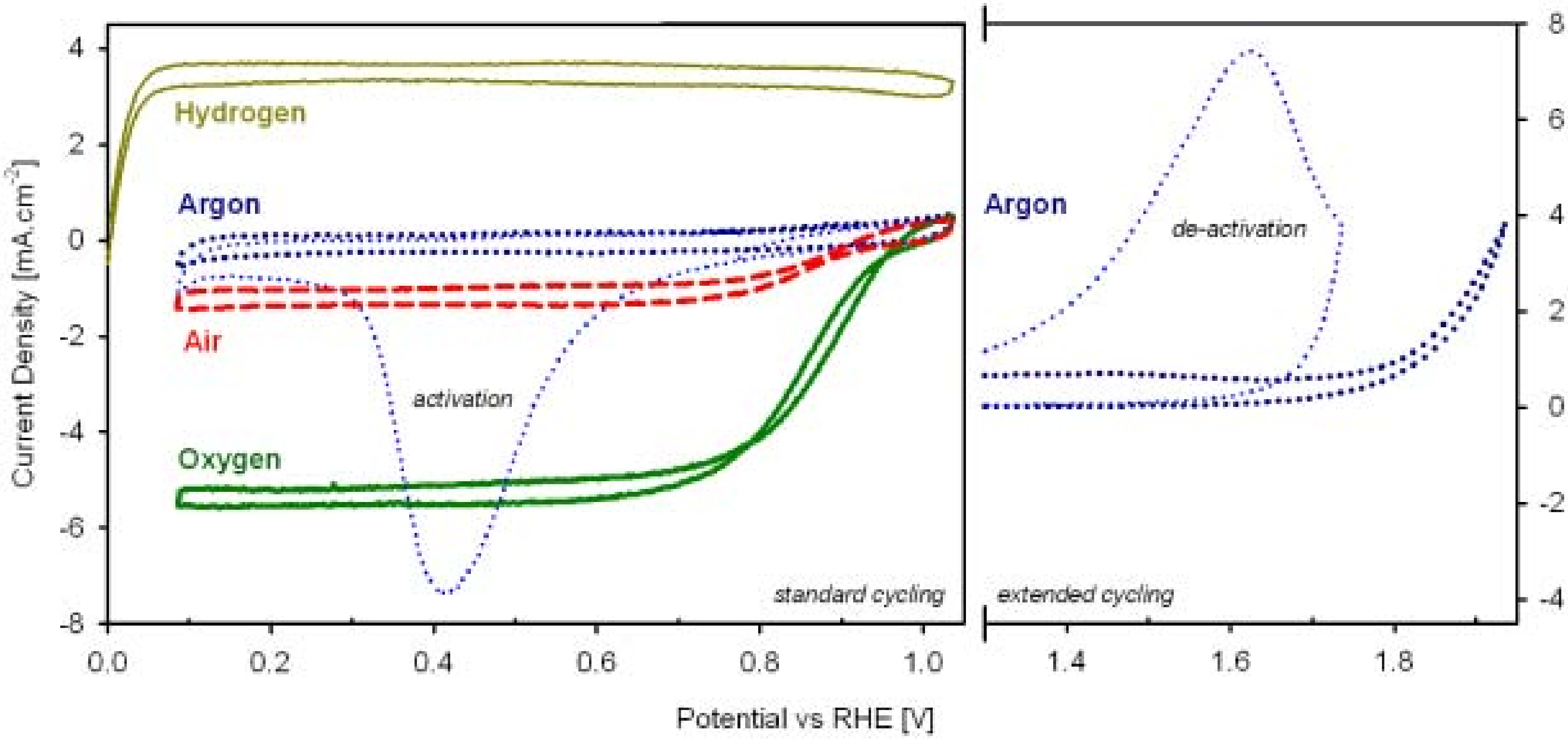
Pt-TaPO highly active for ORR

Tantalum is extremely stable to acid

Doping with Fe, Nb, W, decreases performance

All phosphate catalysts require electrochemical activation

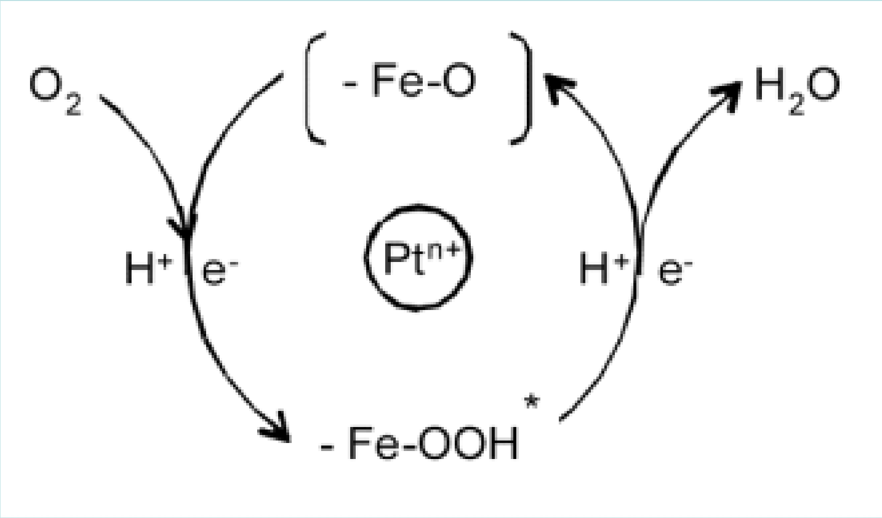
Electrochemical behavior of Pt-Iron Phosphate (Pt-FePO)



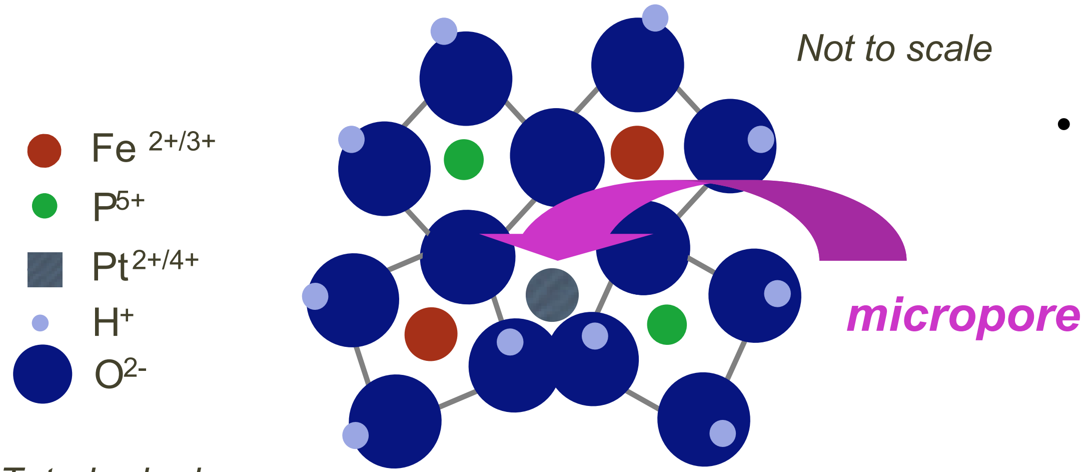
- Electrochemical activation and deactivation processes consistent with the formation of stable hydro-peroxide groups on the surface of the hydrous FePO
  - Observe large reduction peak on first sweep (in O_2 or Ar)
  - Catalysts only deactivated by going to 1.6 V
- All phosphates (with no Pt) also undergo electrochemical activation

Mechanism for Pt-MPO activity
oxygen dissociation on hydroperoxides

$$O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O$$



- Phosphate/oxide facilitates oxygen dissociation to hydroperoxide
  - Metal oxidation states do not change indicating hydroperoxide formation that is charge balanced with oxygen vacancies
  - Pt or other metal critical to mechanism
  - Pt inactive until oxide/phosphate is activated

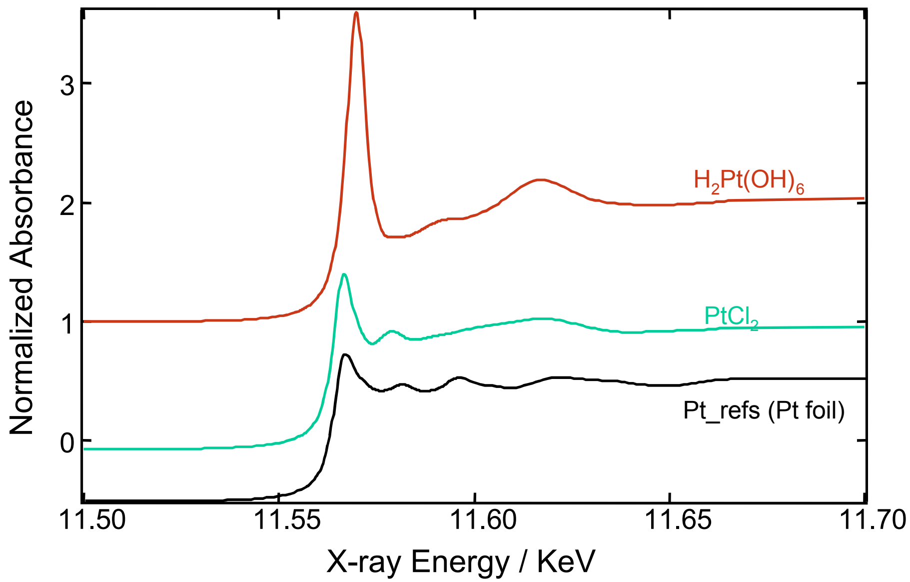


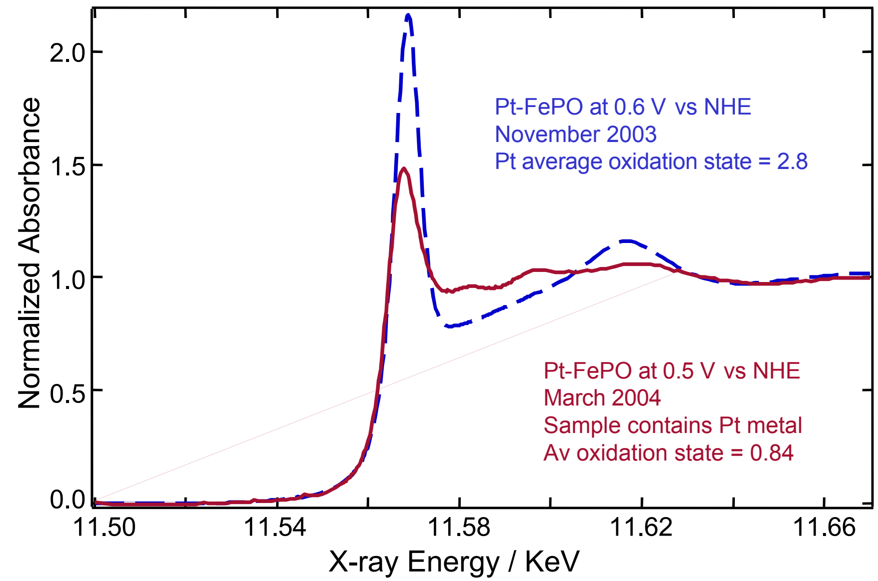
Tetrahedra have short-range order, but no long-range order

- Microporous structure allows access and release of reactants and products
  - Pt ions in pores in a square-planar configuration (from XRD analysis)

Establishing the active state of Pt:

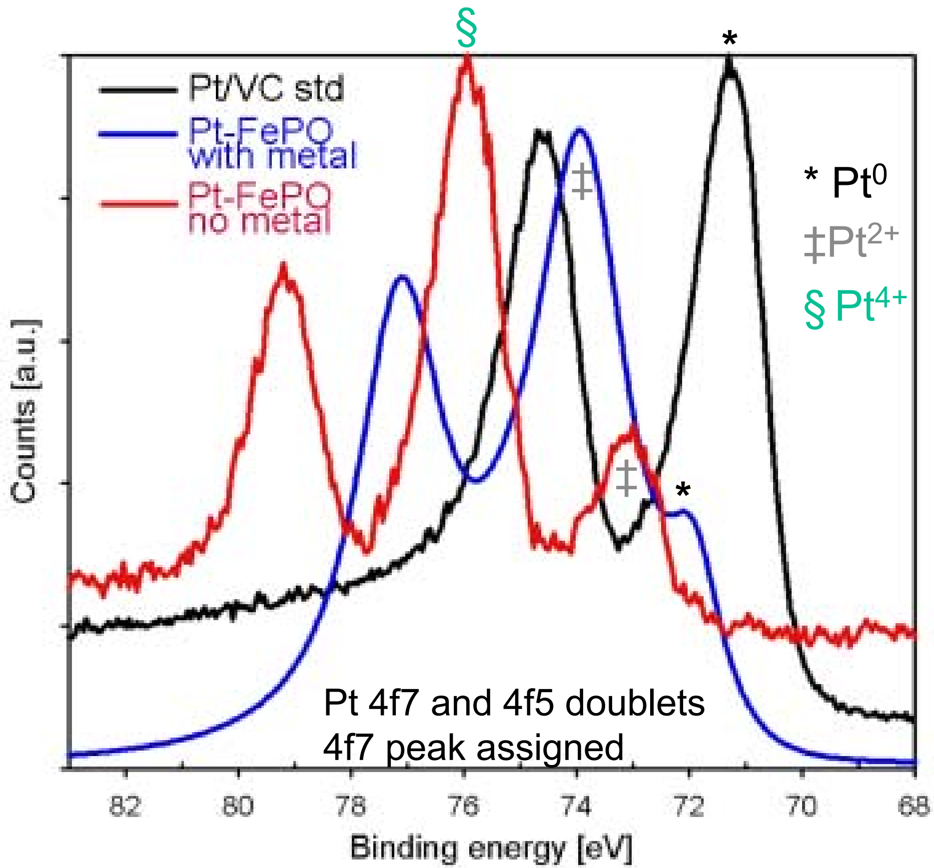
XANES of Pt metal vs. Pt oxide





- Two synchrotron (XANES) runs on in-situ Pt-FePO electrodes (Nov 03, Mar 04)
- Analysis of XANES data by Meitzner (UTEP) and Ramaker (NRL) both show that Pt-FePO used in Nov 2003 probably does not have Pt metal.
- Data from March 2004 run on FePO has a significant amount of Pt metal, but sample was less electrochemically active
- During cycling, the oxidation state of the Pt metal changes as expected, but the Pt oxide changes negligibly
- Ramaker analysis indicates ~6-atom Pt clusters in Pt-FePO from March XANES run
- PDF of XRD shows that no Pt-Pt interactions in active FePO samples (ex-situ).
  - In situ PDF-XRD still needed

Distinguishing between Pt^{2+}, Pt^{4+} and Pt metal



Pt/VC - Pt metal only

Pt-FePO - 2 to 3 types of Pt

XPS analysis on the phosphates can be misleading b/c the acidic supports shift binding energies positive *

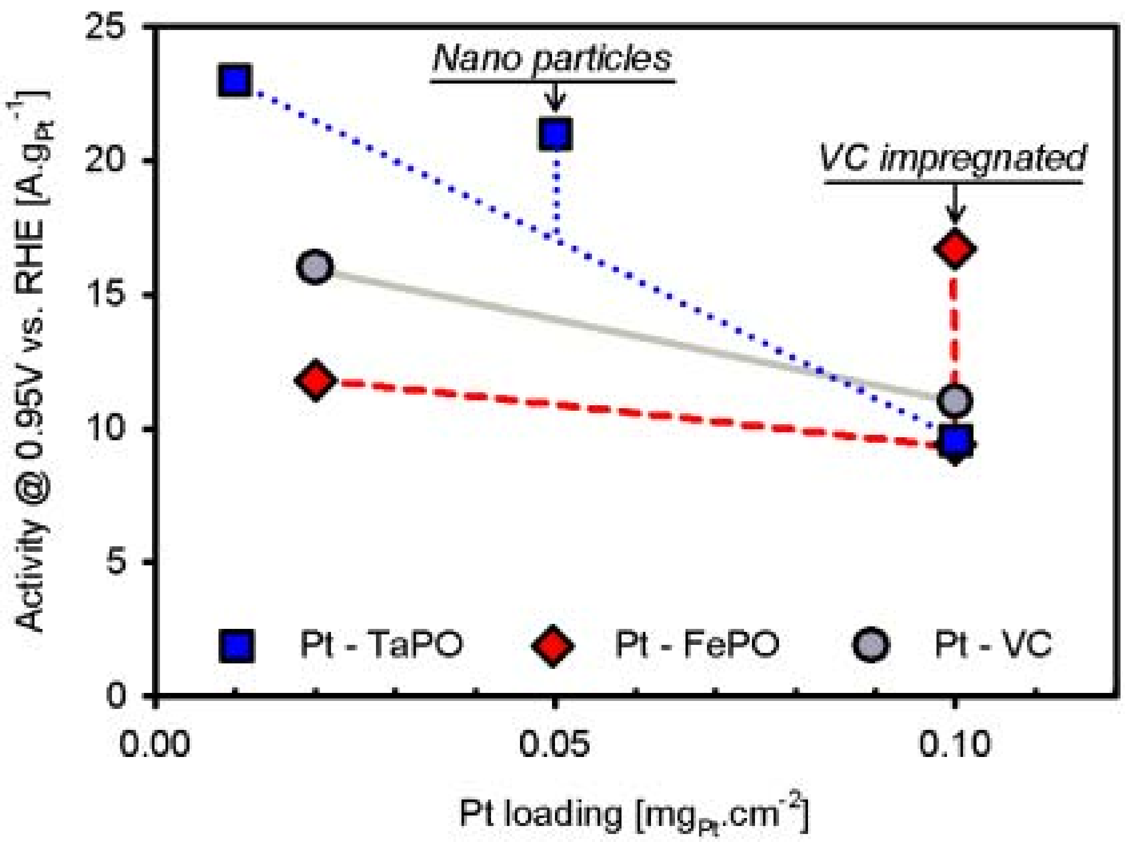
Justification for Pt-metal

- Pt metal is recognized as an excellent ORR catalyst
- Pt metal observed in some XANES runs

Justification for $Pt^{2+/4+}$

- Pt oxides observed in XANES
- Echem of *most active* catalysts show no metallic character
  - No H_2 UPD
  - No CO adsorption
  - No ORR activity until "activated"

Comparative chart of catalyst activities with RDE

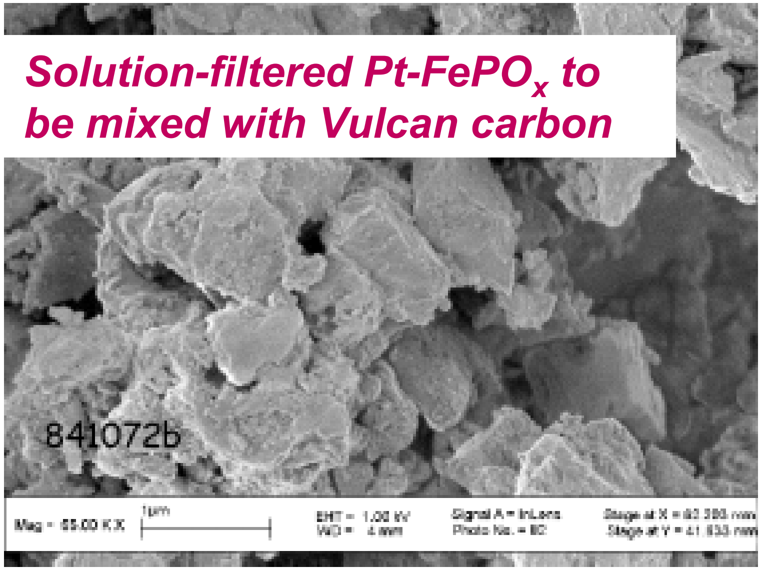


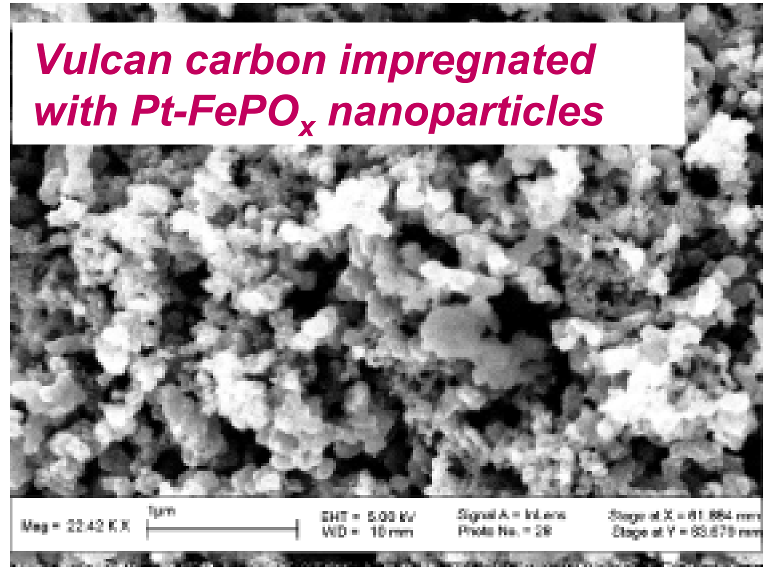
Catalyst activity measured with RDEs in 0.1 M $HClO_4$ at 60 °C and 1600 RPM under oxygen and a sweep rate of 5 mV/s

- Activity of phosphate catalysts are higher than that of Pt-VC only when made as nanoparticles
- Testing at low loadings preferred, but difficult due to issues with paint agglomeration
- Research investment in nanoparticles and nanoparticle dispersions likely to pay off

“Paint” Optimization

Critical for Accurate Catalyst Evaluation





THE CREATION OF HIGH-QUALITY INKS IS NECESSARY FOR HIGH QUALITY ELECTROCHEMICAL ANALYSIS AND SUCCESSFUL INTERACTION WITH INDUSTRY

- Oxide-based inks “clump” if particles are not uniform
- Carbon impregnation methods can lead to high quality inks, but Pt metal may form and the results are less repeatable

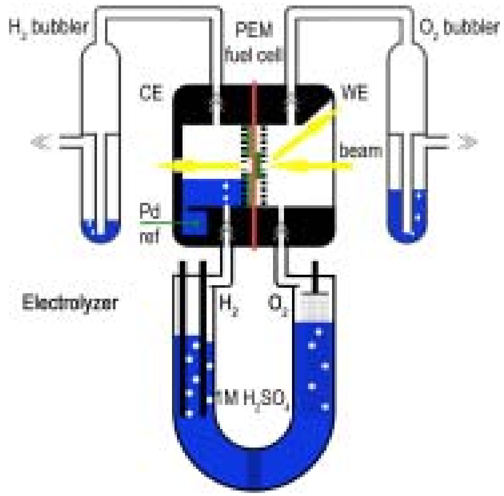
Solution(s)

- Develop new synthetic methods to make uniform nanoparticles
- Evaluate surfactants

Safety

- Follow GLPs (Good Laboratory Practices)
  - Systematic labeling and cataloging of samples
- Fuel cell with electrolyzer developed for use at NSLS for XANES measurements
  - Avoid storage of O_2 and H_2

Potential Issue - safe handling of nanoparticles



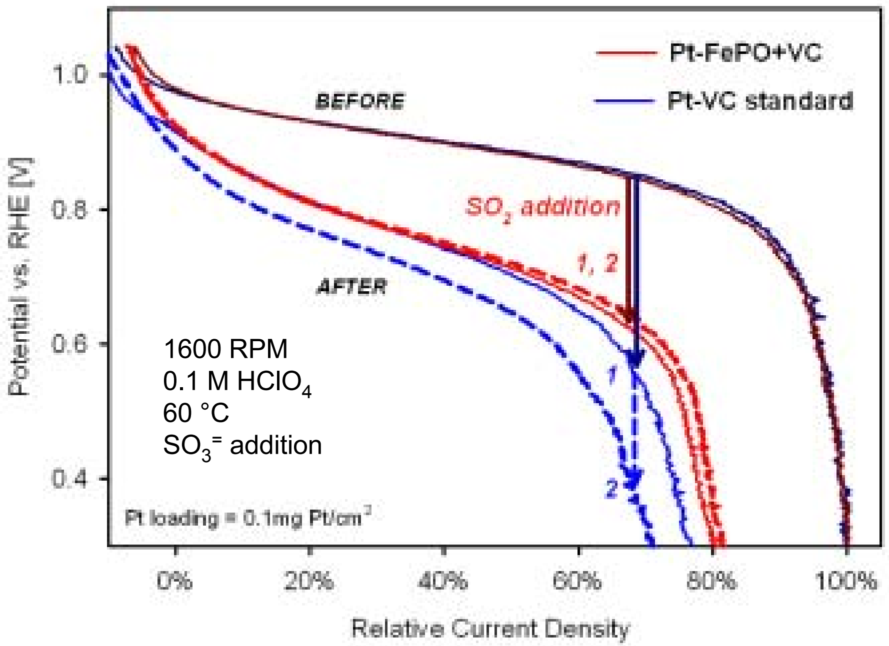
Electrolyzer with fuel cell for safe measurement of in-situ XANES

Response to DOE Tech Barriers

Pt-FePO catalyst maintains performance under SO_2 poisoning while Pt/VC degrades

O: Stack materials cost
(Electrode goal = $5/kW)

- Use lower cost materials to replace Pt



Q: Electrode performance (reduce high overpotentials at cathode)

P: Durability (5000 h)

- Catalysts are stable in sulfuric and phosphoric acid
- Pt distributed in oxides will be less prone to ripening than metallic particles, so there is opportunity for longer lifetime
- Higher tolerance to SO_2 poisoning

Response to reviewers

- ✓ Improve electrochemical methods
- ✓ Quantify progress
- ✓ Justify approach
- ✓ Examine mechanism

What makes this project unique?

- Metal alloys for PEMFCs face:
  - Long-term issues with particle ripening
  - Problems with poisoning
- *Oxide-based catalysts may offer new opportunities as stable and poison-resistant materials*

Interactions and Collaborations

- See collaborators on “Budget” page
  - Dmowski, Chianelli, Ramaker, Meitzer, Schull
- Additional academic interactions
  - Dr. Chris Klug (NRL) - preliminary NMR analysis
  - Dr. Brett Dunlap (NRL) - DFT modeling/simulation

- Interactions with industry
  - RDE and MEA work - Hubert Gasteiger and Shyam Kocha
    - Two visits to GM Fuel Cell Activities since last review

- Signed Materials Transfer Agreements
  - GM Fuel Cell Activities
  - E-TEK
  - Rensselaer Polytechnic Institute

Will be able to establish effective testing program with industry once uniform inks are developed

Concluding remarks accomplishments/progress

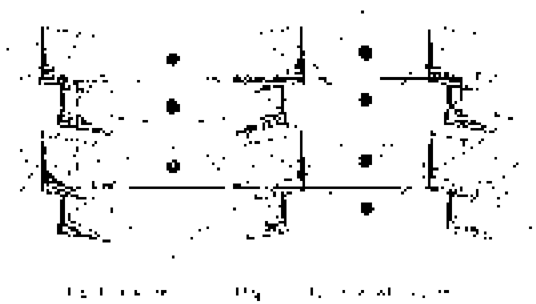
- *Observe 2-3x decrease in Pt loading in phosphate and oxide catalysts vs. Pt/VC standards*
  - Original estimates of activity inaccurate due to poor Pt/VC results
- *There is much room for improvement in catalyst activity if reliable nanoparticles can be synthesized in high quality inks*
  - Increases in activity will proceed with reduction in particle size
- *Mechanism understood to be dependent on a hydroperoxide*
  - Pt metal clusters may also be more active on acid support
  - Understanding role of Pt ions may lead to path for non-Pt catalysts
- *Activity of catalysts linked to structure*
  - Microporous structure is critical for reactant/product mobility
  - Doping experiments yield mixed results
    - Phosphates have lower activity with doping possibly due to changes to bond lengths & no improvement in electronic conductivity (see $LiFePO_4$ literature)
    - Doped tin oxides may become more electronically conductive

Future work

- Continue on path to develop stable, low-Pt and non-platinum catalysts
- Develop reliable synthetic procedures & inks
  - Implement methods to control nanoparticles
    - Ion exchange of tantalum phosphates
  - Probe impact of synthesis on catalyst performance
  - Establish methods for uniform dispersion of particles
- Identify active sites in catalyst
  - Repeat in situ XANES experiments and correlate to XPS
  - Examine catalysts in-situ with XRD
    - Key issue is to reduce measurement time

WISH LIST

- *DFT calculations*
- *NMR - in situ and ex situ*



Murashova EV, et al, *Inorg. Mater.* ***39***, 1303, **2003**

PUBLICATIONS:

1. Bouwman, et al, Platinum-iron phosphate electrocatalysts for oxygen reduction in PEMFCs," *JECS*, in press.
2. Bouwman, et al, Platinum-iron phosphate catalyst for oxygen reduction," in Advanced Materials for Fuel Cells and Batteries -- G. Ehrlich, ECS Orlando, 2003.
3. Dmowski, et al, "Atomic structure of disordered Pt-Ru black and Pt-iron phosphate electrocatalysts," ibid.